Molecular Dynamics Simulations in the Grand Canonical Ensemble (Invited)

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An extended Hamiltonian technique for performing grand canonical ensemble molecular dynamics (GMD) simulations is described. The Hamiltonian includes a continuous particle number variable that is the sum of the integer particle number and a coupling parameter. The coupling parameter varies between zero and one and scales the fractional particle's interactions with the rest of the system. Equations of motion for the coupling parameter are derived from the Hamiltonian and integrated to yield particle number fluctuations at constant chemical potential. The method is distinct from other extended-system approaches in that a bias potential for umbrella sampling is used to flatten the free energy surface between integer particle number states. GMD simulations have been used to predict the dependence of density on chemical potential for the extended simple point charge water model. Results are in agreement with several independent calculations. The method has also been adapted for investigations of 2:1 clay minerals where the interlayer environment consists of an aqueous ionic solution in small (< 10 AA) slit pores. These investigations are related to swelling and ion exchange phenomena in 2:1 clay minerals.